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1. Introduction

Nitrous oxide (N_2O) is a powerful greenhouse gas (GHG) which accounts for 8 % of total global GHG emissions (Reay et al., 2012) and has a global warming potential 298 times greater than that of CO_2 (Forster et al., 2007). The breakdown of N_2O to NO in the stratosphere also results in the depletion of stratospheric ozone (Crutzen and Lelieveld, 2001). Although N_2O is a naturally occurring gas, there has been an increase in atmospheric concentration of 16 % since 1750 which is primarily attributed to emissions from fertilized agricultural soils (Davidson, 2009). Global annual emissions from agricultural soils are currently estimated to be around 4 Tg N_2O-N (Reay et al., 2012).

The production of N_2O by fertilised arable soils is associated with the application of inorganic N fertilisers and manures or soil disturbance, which cause an increase in soil concentrations of ammonium (NH_4^+) and nitrate (NO_3^-); which is responsible for the subsequent production of N_2O as a byproduct of the microbial processes of nitrification and denitrification (Chapuis-Lardy et al., 2007; Inselbacher et al., 2011). Emissions from fertilised soils have high spatial and temporal variability (Flechard et al., 2007; Lilly et al., 2003) due to the influence of multiple factors such as soil water filled pore space (WFPS), soil compaction, pH and temperature on the N_2O source processes (Bessou et al., 2010; Castellano et al., 2010; Pierzynski et al., 2005; Smith et al., 2003). The high spatial and temporal variability of N_2O emissions from agricultural soils

makes it difficult to accurately assess annual fluxes. It has been suggested that a solution to this problem is the use of high frequency long path length measurement techniques such as eddy covariance (Flechard et al., 2007). However, such methods require large areas and are typically of limited value in plot based field experiments where manipulation treatments are compared, and emission factors (EFs) need to be calculated (as an unfertilised control area is needed too). An alternative approach, used in this study, is the use of static chambers with high temporal and spatial replication (Chadwick et al., 2014). Previous studies of N_2O emissions from agricultural soils using the static closed chamber technique often involved the use of only a small number of replicate chambers per treatment and a low sampling frequency over a short period of time. For example, a number of studies have used six or less static chambers per treatment (Ball et al., 1999; Clayton et al., 1997; Dobbie et al., 1999; Dobbie and Smith, 2003; Smith et al., 2012). Previous studies have also often been based on short measurement periods ranging from 5 days to 6 weeks after fertiliser application (Skiba and Ball, 2002; Skiba et al., 2002; Smith et al., 2012). Furthermore, previous studies have not always adequately captured temporal dynamics where gas samples were taken at intervals of 2-4 weeks (Rees et al., 2013).

The relationship between the amount of N fertiliser applied and the magnitude of N_2O emissions is quantified through the use of an EF (EF1) which expresses the quantity of N_2O-N emitted as a proportion of the N fertiliser applied. The EF calculation also accounts for background emissions which are largely due to mineralisation of crop residues (IPCC, 2006). Bouwman (1996) reviewed experiments of at least a year in length and recommended an EF (EF1) of 1.25 % of the N applied to express the relationship between applied N fertiliser and N_2O emissions. The IPCC subsequently used this as a "default EF" to enable calculation of countries' N_2O emissions from soils receiving inorganic fertiliser N (IPCC, 1996). This value has since been revised downwards

64 on the basis of more recent evidence to give an EF of 1 % of N applied for use in the Tier 1
65 methodology for calculating N_2O emissions (IPCC, 2006). However many countries including
66 the UK have not yet adopted the 1 % EF in their national inventory calculations. This default EF
67 attempts to estimate typical emissions across large spatial areas and time periods, however there
68 is concern that local soil and climatic conditions, and the type and rate of fertiliser used can lead
69 to significant variance from average conditions (Smith et al., 2012). The use of a 1.25 % EF has
70 been controversial in Scotland where it has been demonstrated that large changes in soil WFPS
71 may result in Scottish EFs which are atypical of the whole of the UK (Dobbie et al., 1999;
72 Dobbie and Smith, 2003). This is reflected in calculated N_2O EFs ranging from 0.17 – 7 % for a
73 range of N sources for Scottish agricultural soils (Clayton et al., 1997; Dobbie et al., 1999; Smith
74 et al., 1998a). To improve the accuracy of agricultural N_2O reporting it is necessary for
75 investigation into the effects of controlling variables on N_2O emissions and the appropriateness
76 of utilising a 1.25 % EF, or the new 1 % EF, regardless of location, and this is particularly
77 relevant in areas of the UK which may experience extreme or unusual climatic conditions.

78

79 Mitigation of agricultural N_2O emissions is necessary if we are to limit the contribution of
80 agriculture to climate change. The use of nitrification inhibitors (NIs) such as dicyandiamide
81 (DCD) which act to decrease N_2O emissions by deactivating the ammonia monooxygenase
82 enzyme used in the primary stage of nitrification (Amberger, 1989) have proved successful in
83 mitigating agricultural N_2O emissions (Di and Cameron, 2003; Di et al., 2007) and have also
84 demonstrated the potential to increase crop yields (Abalos et al., 2014). However, there has been
85 little investigation into the effectiveness of DCD in UK agricultural systems and more research
86 in this area is required. Another N_2O mitigation option which requires further investigation is the

use of split applications of N fertiliser. Split applications result in the application of smaller individual doses of fertiliser, which reduces surplus N in the soil and decreases the potential for loss of N via transformation to N_2O or leaching, in addition to being more suitable for crop requirements (Burton et al., 2008), potentially increasing the nitrogen use efficiency of fertilisers. Reducing the amount of surplus N is an important method of decreasing N_2O emissions as it not only has positive impacts on the environment but is also financially beneficial for the farmer. Altering the amount or type of fertiliser applied is another means by which surplus N may be decreased, and research has indicated that the use of urea rather than ammonium nitrate (AN) fertiliser may result in lower N_2O emissions (Dobbie and Smith, 2003; Smith et al., 2012).

Although it is important to minimise N_2O emissions from agricultural soils, it will also be necessary in the future to produce greater quantities of food, meaning that crop yield must not be negatively impacted by mitigation options. Emission intensities i.e. the amount of N_2O produced per unit of crop yield, are therefore a vital indicator of the potential of any N_2O mitigation option (Van Groenigen et al., 2010), although research into this area has thus far been limited.

This work forms part of a nationwide project to assess the effect of a range of organic and inorganic nitrogen fertiliser treatments on N_2O emissions from agricultural soils with the results being used to improve agricultural management systems and to reduce uncertainty in the UK agricultural greenhouse gas inventory (GHG, 2013). More specifically, the aims are to:

i). Compare N_2O emissions, calculated EFs and emission intensities from different inorganic fertiliser treatments

ii). Investigate the efficacy of potential N_2O mitigation options.

iii). Assess the appropriateness of the use of the standard 1.25 % or 1 % EF for the area under investigation.

2. Materials and Methods

2.1 Site description

The experiment began in April 2011 at Gilchriston in south east Scotland (Grid reference: NT479658). Gilchriston is a commercial arable farm, selected for its location in one of the principal geoclimatic zones which support arable production in the UK. The site characteristics are described in Table 1. Soil pH, organic matter and bulk density were calculated using field measurements, other soil information was obtained from Hipkin (1989).

2.2 Experimental design

Nitrogen fertiliser treatments were compared that ranged from a control (0 kg N ha^{-1}) to 200 kg N ha^{-1} and included the recommended application rate for the area of 120 kg N ha^{-1} (Defra, 2010). The fertiliser was applied either in the form of ammonium nitrate (AN) or urea. Fertiliser was applied in two doses (three doses for one treatment) in April and May 2011, by hand to the entire plot, to simulate agronomic practice. The NI DCD was applied at a rate of 10 kg ha^{-1} as a spray an hour after the application of AN and urea. Further details of treatments are presented in Table 2. The experimental layout consisted of 10 m x 3 m plots replicated three times for each treatment in a randomized block design. For the duration of the experiment, pesticides were applied according to standard recommendations, and P_2O_5 and K_2O were applied to all plots at rates of 60 kg ha^{-1} and 90 kg ha^{-1}, respectively, in order to satisfy crop demand.

2.3 Gas and soil sampling, measurements and analysis

Nitrous oxide fluxes were measured at the experimental site over a one year period (7th April 2011 – 30th March 2012) using the static closed chamber technique (Chadwick et al., 2014; Clayton et al., 1994) and with a methodology that was consistent with Global Research Alliance guidelines (de Kleine and Harvey, 2012). Although the N_2O results are referred to as "annual" emissions, the precise number of days this period represents is 358 days. The intense N_2O sampling frequency was based on the assumption that most of the total direct N_2O emissions occur within the first month following each dose of fertiliser application (Dobbie et al., 1999). The sampling strategy therefore involved around 50 % of the total N_2O measurements occurring during this period of expected high emissions in order to capture the variations between treatments.

Five circular chambers made of opaque polypropylene (200 mm diameter, 300 mm height and soil surface area coverage of approximately 0.126 m^2) were installed per plot, resulting in the use of 15 chambers per treatment. Chambers were installed by cutting a 5 cm deep slot into the soil and inserting the base of the chamber into this slot. Soil was tightly packed around the base of the chamber (on the outside) to ensure a good seal. The chambers were left in place for the whole experiment except when agricultural operations such as harvest deemed removal necessary. Extensions were added to the tops of the chambers during the growing season in order to avoid damaging the plants within the chambers. On each sampling occasion, aluminium lids were clipped onto the top of each chamber and the chamber remained covered for 40 minutes. The headspace was then sampled through a small sampling port in the lid using a syringe and gas samples were transferred to pre-evacuated 20-22 ml glass vials. Ambient and 'linearity check' gas samples were also collected. The linearity check involved collecting samples at 10 minute

intervals from 3 randomly selected chambers (1 from each block) throughout the sampling period. Sampling was conducted between 10:00 and 12:00 h to ensure consistency. See Chadwick et al. (2014) for further methodology information.

Gas samples were analysed for N_2O concentrations using an Agilent 7890A Gas Chromatograph (GC) fitted with an electron capture detector (Agilent Technologies, Berkshire, UK) and a CTC Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK). The GC response was calibrated using certified N_2O gas standards (0.35, 1.1, 5.1, 10.7 ppm) and the N_2O limit of detection was 0.025ppm. Air temperature was recorded on every N_2O sampling occasion and chamber height was also measured for use in N_2O flux calculations. Daily N_2O fluxes were calculated using linear regression which assumes a linear increase in N_2O concentration in a known volume over a known period of time, and the ideal gas law (Saggar et al., 2008). Cumulative N_2O fluxes from each chamber were calculated using the trapezoidal rule (area under the curve) to interpolate fluxes between sampling points. For each treatment, cumulative fluxes were calculated using the mean of the 5 chambers per plot, in order to calculate a treatment mean cumulative emission value and associated standard error.

Composite soil samples consisting of five cores (0-10 cm depth) collected at random locations using a 30 mm diameter auger were taken from each block on each N_2O sampling occasion for soil gravimetric water content (GWC) determination, i.e. one soil moisture content measurement per block on each occasion. Composite soil samples from each plot were also collected in this way at approximately monthly intervals throughout the one-year experiment for soil mineral N content determination, i.e. generating one sample per plot. Fresh soil samples were sieved

(<4mm) and extracted using 2M KCl (soil to extractant ratio 1:2) for determination of soil ammonium (NH_4^+-N) and nitrate (NO_3^--N) contents using a Skalar San^{++} continuous flow autoanalyser (Skalar, York, UK). Soil bulk density was determined for each block through collection of intact soil samples using metal rings on frequent occasions throughout the experiment. Soil bulk density and GWC were used to calculate soil WFPS (%) on each gas sampling occasion (Robertson, 1999).

A meteorological station at the site recorded daily rainfall. Air and 10-cm depth soil temperatures were also recorded using a temperature probe (RS Components, Northamptonshire, UK) on each N_2O sampling occasion.

The crop was harvested on 22nd August 2011 using a small plot harvester which harvested an area of 15m^2 from each plot. Just prior to harvest, a random sample of 100 tillers per plot was also collected by hand. This was threshed and weighed to determine the ratio of grain to straw and chaff. The % dry matter and N content of the grain, and the mixed straw and chaff, from each plot was determined.

2.4 Emission Factor calculation

Emission factors, which express the N_2O-N emitted from each treatment as a percentage of the total N applied, were calculated (subtracting control values from each of the 3 blocks from corresponding treatment values as appropriate before calculating mean treatment EFs) using the following equation:

$$EF = \left(\frac{Cumulative\ \ annual\ N_2O flux\ (kg\ N_2O\text{-}N) - cumulative\ annual\ N_2O\ flux\ from\ control\ (kg\ N_2O\text{-}N)}{N\ applied\ \ (kgN)}\right) \times 100$$

194 EFs were calculated for three separate timescales: 1). An annual EF was calculated as
195 recommended by Bouwman (1996). 2). A "seasonal" EF was calculated which included N_2O
196 data up until harvest to take into account the effects of crop growth on N_2O emissions and the
197 time taken for soil mineral N levels to return to "background" levels. 3). A "five week" EF was
198 calculated for the 5 weeks following the first fertiliser application. This time scale was chosen as
199 it has been reported that the majority of emissions take place during the 4 weeks following
200 fertiliser application (Dobbie et al., 1999) and would therefore enable clearer identification of
201 treatment effects. However, due to dry weather during this period there were very low N_2O
202 emissions from all treatments, so it was extended to 5 weeks to include the large peak in
203 emissions which occurred during May.
204
205 *2.5 Statistical analysis*

206 Statistical data analyses were carried out using Genstat (16.1). The occurrence of any significant
207 differences in measurements between treatments was tested using one-way analysis of variance
208 (ANOVA) with blocks. Data were checked for normality before ANOVAs were applied and
209 analysis of residuals was used to determine outliers. Two outliers were identified during the
210 analysis of the cumulative N_2O data and the annual and seasonal EFs, these were from blocks 2
211 and 3 of the AN 40 treatment. These outliers were subsequently excluded from the analysis.
212 Treatment effects were deemed significant if $p \leq 0.05$. Regression analysis was performed to
213 determine the relationship between nitrogen applied and the cumulative annual emission. The
214 REML procedure was used for this analysis with nitrogen level, specified as a variate, as the
215 fixed factor, and the block was specified as the random factor. REML regression was also used
216 to analyse the relationship between the daily N_2O emissions and the % WFPS with the block

specified as the random factor. In this case, the emissions were transformed using natural logarithms. Due to large negative emissions, 25 g N_2O-N ha^{-1} d^{-1} was added to the emissions before transformation. On analysis of the residual plots, one outlier was identified and removed from the analysis (Block 2 on 7th July).

3. Results

3.1 Nitrous oxide fluxes

Nitrous oxide fluxes showed high temporal variation with most emissions occurring during a few intermittent flux episodes, and also varied widely between treatments (Figure 2). Emission maxima of 170-190 g N_2O-N ha^{-1} d^{-1} from the AN 160 and AN 200 treatments occurred 13 days after the second fertiliser application in May 2011. Total N_2O emissions were higher in August than any other month with a maximum cumulative monthly value of 0.013 kg N_2O ha^{-1} from the CON treatment. Negative N_2O fluxes were occasionally observed during the experimental period with the largest negative flux of -18 g N_2O-N ha^{-1} d^{-1} occurring for the AN 80 and urea 120 + NI treatments in July.

Cumulative N_2O emissions for the one year study period showed marked treatment effects (Figure 3), with a general increase in cumulative N_2O emissions associated with larger N applications. During the 1 way ANOVA with blocks, 2 outliers were observed from the analysis of the residuals. These were the cumulative emissions from blocks 2 and 3 of the AN 40 treatment and these were subsequently removed from the analysis. Maximum cumulative emissions were recorded from the AN 200 treatment with a value of 3.82 kg N_2O ha^{-} [1.] Cumulative emissions from the AN 200 treatment were significantly higher ($p=0.009$. SED =

239 0.605) than from the CON, urea 120, urea 120 + NI, AN 120 + NI, AN 40 and AN 80 treatments.
240 The lowest cumulative N_2O emissions were from the Urea 120 + NI treatment with a value of
241 1.32 kg N_2O ha^{-1}. This was a non significant 45 % reduction in cumulative emissions in
242 comparison to the urea 120 treatment. There was a significant 38 % decrease in cumulative
243 emissions from the AN 120 + NI treatment in comparison to the AN 120 treatment; however
244 there was no significant difference between the AN 120 + NI and that AN (3 splits) . Cumulative
245 N_2O emissions from the AN (3 splits) and urea 120 treatments showed a trend for lower
246 emissions than from the AN 120 treatment by 11 % and 26 %.

247

248 *3.2 Environmental conditions*

249 The weather during the experimental period was atypical for this region, with a dry spring,
250 followed by an unusually wet summer which coincided with low temperatures (Figure 1a and b).
251 The high N_2O emissions observed during the summer corresponded with the occurrence of most
252 of the large rainfall events during this period (Figures 1 and 2). The May emission peak occurred
253 in a relatively dry period (the soil WFPS was 38 %) but during the peak in emissions in August
254 the soil was considerably wetter (soil WFPS values of ~50 %). Despite the high rainfall, only 4
255 % of the measurement days had 50-70 % WFPS with all of the remaining days having < 50 %
256 WFPS. A WFPS value of >60-70 % is generally associated with denitrification conditions, and
257 hence with greater N_2O fluxes (Davidson, 1991).

258 *3.3 Emission factors*

259 Emission factors for each time period (annual, seasonal and 5 weeks) were calculated (Table 2).
260 The maximum annual EF was 1.35 from the AN 120 treatment and the mean annual EF was

261 0.69, in comparison to the mean seasonal EF of 0.40 and the mean 5 week EF of 0.44. Two
262 negative EFs were obtained for the annual and seasonal urea 120 + NI treatment. These represent
263 positive emissions which are lower than the unfertilised control due to the EF calculation method
264 used, in which control fluxes are subtracted from treatment fluxes. There were no significant
265 differences between EFs for all treatments at any of the three timescales (EF annual, p=0.082; EF
266 seasonal, p= 0.082; EF 5 wk, p = 0.209).

267 *3.4 Soil mineral N*

268 Soil NO_3^--N and NH_4^+-N concentrations increased following fertiliser application with a peak in
269 NO_3^--N concentration of 68 kg N ha^{-1} in the AN 200 treatment and a peak in NH_4^+-N
270 concentration of 57 kg N ha^{-1} in the urea 120 + NI treatment, just over a month after the final
271 fertiliser application (Figure 4). As expected the mineral N concentrations increased as the
272 application rate of AN fertiliser increased. The NI treatments acted to significantly increase
273 NH_4^+-N concentrations ($p< 0.05$) and significantly decrease NO_3^--N concentrations ($p<0.05$) in
274 comparison to the non-NI amended treatments. Following peak soil NO_3^--N and NH_4^+-N
275 concentrations, values decreased to < 5 kg N ha^1. The concentrations of both NO_3^--N and NH_4^+-
276 N were consistently below 5 kg N ha^{-1} in the period between August 2011-March 2012.

277

278 *3.5 Crop yield and yield scaled emissions*

279 Crop yield (grain harvest at 15 % dry matter) ranged from a minimum of 1.46 t ha^{-1} for the
280 control treatment to 9.30 t ha^{-1} for the AN 200 treatment (Figure 5a). Significantly greater crop
281 yield was obtained from the AN 160 and AN 200 treatments ($p<0.001$, SED = 0.1682) than
282 from all other treatments. The crop yield obtained was dependent on the amount of N fertiliser

applied, with greater crop yield obtained for larger applications of N fertiliser. Crop yield was significantly decreased by 9 % and 10 %, respectively for the AN 120 + NI and the urea 120 + NI treatments in comparison to their non NI amended counterparts and there was significantly lower crop yield from the AN (3 splits) treatment in comparison to the AN 120 treatment. Yield scaled emissions generally decreased with increasing rates of N fertiliser application from a maximum of 1.15 kg N_2O ton^{-1} grain for the control treatment, to a minimum of 0.18 kg N_2O ton^{-1} grain for the urea 120 + NI treatment (Figure 5b). There was a significant effect of treatment on yield scaled emissions ($p=0.002$, SED=0.1742) which showed that the control treatment had significantly higher emission intensities than the fertiliser treatments.

4. Discussion

4.1 Linearity of N_2O emissions with N application

This study demonstrated the value of a high intensity sampling strategy in assessing variability in N_2O emissions between fertiliser treatments. Greater applications of N fertiliser generally resulted in higher cumulative N_2O emissions due to the increase in soil NO_3^- and NH_4^+ contents. There was a strong linear relationship ($p<0.001$) between the amount of N fertiliser applied and the magnitude of the cumulative N_2O emissions (Figure 6). Treatments AN 80 and AN 120 demonstrated smaller variability in N_2O emissions between blocks in comparison to the other treatments. The IPCC Tier 1 EF approach assumes that N_2O emissions are a linear function of N application (Philibert et al., 2012) and our results support this assumption, in contrast to some suggestions that the relationship between N input and N_2O emissions may be non-linear (Hoben et al., 2011; McSwiney and Robertson, 2005).

4.2 Cumulative N_2O emissions and environmental controls

Cumulative annual emissions from all treatments were particularly high in comparison to comparable experiments in this area. McTaggart et al. (1997) and Smith et al. (1998a) measured N_2O emissions from spring barley crops fertilised with 120 kg N ha^{-1} in South East Scotland in 1993 and 1994-1995 respectively and reported emissions of 0.8 kg N_2O-N ha^{-1}, considerably lower than the 3.28 kg N_2O-N ha^{-1} reported for the AN 120 treatment from our experiment. The lower frequency of measurements carried out by McTaggart et al. (1997) and Smith et al. (1998a) may explain their reported lower emissions. The high emissions observed during this experiment contrasts with work by Smith et al. (1998a), which reported that emissions from Scottish sites were generally small due to low spring and summer temperatures which reduces the production of N_2O. Most of the N_2O emissions are expected to occur in the four weeks following fertiliser application (Bouwman, 1996) and the mean soil temperature recorded during this period for our experiment was 13.3 °C, only 0.6 °C lower than the maximum mean monthly soil temperature observed in July which will have promoted high N_2O production.

Previous work by Dobbie et al. (1999), Flechard et al. (2007), Jones (2007) and Rees et al. (2013) has demonstrated that the key factors affecting N_2O emissions from N fertilised agricultural soils are % soil WFPS, soil temperature and soil mineral N. However, there are threshold levels of these factors and if this threshold is not exceeded by any of these variables then N_2O production may be limited (Dobbie and Smith, 2003; Topp et al., 2013). During the period immediately following fertiliser application and the subsequent summer months when soil mineral N contents and temperature were not limiting to N_2O production, the primary variable affecting emissions was % soil WFPS . This limiting effect was clearly demonstrated in this experiment in the period between the first fertiliser application and the large peak in emissions

approximately four weeks later. During this period the mean soil temperature of 13°C would not have been limiting to N_2O production, however, low % soil WFPS would have been (Figures 1 and 2). A large rainfall event in early May (Figure 1) increased % soil WFPS from a mean value of 27 % to 39 % which increased N_2O emissions (Figures 1 and 2). During the peaks in N_2O emissions in August, % soil WFPS values were approximately 46 % (Figures 1 and 2), however, at this time soil mineral N had returned to below what is considered a threshold level of 5 mg N kg^{-1} (5.95 kg N ha^{-1}), which implies that soil WFPS has greater control over the potential for N_2O production than soil mineral N contents. The relationship between flux response and % soil WFPS was analysed for the highest N fertiliser treatment for this experiment. When N_2O data from the one year measurement period is used, including periods in which soil NO_3^- is below 5 mg N kg^{-1}, there is a significant positive relationship between N_2O and soil WFPS ($p<0.001$) (Figure 7a). When periods in which soil NO_3^- <5 mg N kg^{-1} are removed (Figure 7) there is also a significant positive relationship between N_2O and soil WFPS ($p<0.001$) (Figure 7b), in agreement with Dobbie et al. (1999) who also found a significant relationship ($p<0.05$) when the same limitations were applied.

The observation of a significant relationship between N_2O emissions and % soil WFPS, even when soil NO_3^- was < 5mg N kg^{-1} is in contrast to previous studies of Scottish arable sites which found no relationship between these variables below an NO_3^- threshold of 5mg N kg^{-1} (Clayton et al., 1997; Dobbie et al., 1999; Smith et al., 1998a). The relationship between N_2O flux and % soil WFPS is related to the dominance of either nitrification or denitrification as the N_2O producing processes. Davidson (1991) suggested that denitrification predominates at soil WFPS >60 % and that at values <60 %, nitrification is the dominant process. In this study, despite greater than average annual rainfall, the 60 % WFPS threshold was never exceeded. This

351 combined with the return of NH_4^+ concentrations to background levels prior to the NO_3^-
352 concentrations suggests that nitrification may have been the dominant N_2O production process.

353

354 *4.3 Emission intensities*

355 Crop yield increased with increasing rates of AN fertiliser application as expected due to the
356 greater availability of NO_3^- and NH_4^+ in the soil for uptake by the growing crop. However, it is
357 important to consider the amount of N_2O produced per unit of yield (yield scaled emissions, or
358 yield intensity). This allows assessment of a greater part of the treatment's "life cycle" than just
359 taking into account N_2O emissions, as ultimately for a fertiliser to be financially viable it must
360 produce sufficient crop yield. The recommended fertiliser application rate of 120 kg N ha^{-1},
361 which was used in this experiment had yield scaled emissions of 0.39 kg N_2O ton^{-1} grain. The
362 optimum fertiliser application rate would produce a high crop yield but minimal N_2O emissions,
363 and the results of this experiment demonstrate that the optimum fertiliser application would be
364 AN 160 kg N ha^{-1}. This application rate provided a higher crop yield than the 120 kg N ha^{-1}
365 application rate, but lower N_2O emissions, resulting in lower yield scaled emissions of 0.35 kg
366 N_2O ton^{-1} grain. Yield scaled emissions decreased with increasing rates of N fertiliser
367 application at low application rates from 1.15 kg N_2O ton^{-1} grain for the control treatment to 0.28
368 kg N_2O ton^{-1} grain for the AN 80 treatment. Although the yield scaled emissions from the AN 80
369 treatment are relatively similar to the yield scaled emissions from the optimum AN 160
370 treatment, it must be considered that crop yields from the AN 160 treatment are 40 % higher,
371 therefore it is advantageous to produce greater crop yields whilst not significantly increasing
372 yield scaled emissions. The yield scaled emission results obtained are in contrast to the results of

373 a meta analysis carried out by Van Groenigen et al. (2010), which reported the lowest emission
374 intensities following N application of 180-190 kg N ha^{-1}. We found no significant difference in
375 yield scaled emissions from applications of 40 -200 kg N ha^{-1} despite significantly greater crop
376 yields at N application rates of 160 and 200 kg N ha^{1}. Our yield scaled emission results indicate
377 that we must avoid under fertilising crops if we are to minimise the risk of enhancing N_2O
378 emissions whilst simultaneously obtaining poor crop yields.

379 *4.4 Mitigation option effects on N_2O emissions and crop yield*

380 The decrease in N_2O emissions through the use of the NI (DCD) is an important finding of this
381 research. The use of DCD has proven effective in reducing N_2O emissions in previous studies
382 conducted on grassland and spring barley sites in New Zealand and the UK (Di and Cameron,
383 2002, 2003; Di et al., 2007, 2010; McTaggart et al., 1997). However little work has been
384 undertaken to examine the effectiveness of DCD on arable soils in Scotland. A previous field
385 study in the UK investigating the effectiveness of DCD in reducing N_2O emissions from N
386 fertilised arable crops found a 36 % reduction in emissions from spring barley when DCD was
387 used (McTaggart et al., 1997). The successful inhibition of nitrification by DCD in this study is
388 evident due to the significantly increased levels of NH_4^+-N in the soils from the NI treatments
389 and decreased soil NO_3^--N contents, in combination with the decreased N_2O emissions. DCD
390 was more effective in reducing emissions from the AN 120 + NI treatment than from the urea
391 120 + NI treatment. This is in contrast to previous work which has demonstrated greater
392 decreases in N_2O emissions when DCD was applied to urea fertilised soils in comparison to AN
393 fertilised soils (McTaggart et al., 1997), as would be expected due to the higher quantities of soil
394 NH_4^+-N found in the urea treatment.

395 The potential of a 3 split AN fertiliser application and urea application (urea 120) to decrease
396 cumulative N_2O emissions in comparison to the AN 120 treatment was also apparent as
397 emissions were significantly decreased by 11 % and 26 % respectively. The decrease in N_2O
398 emissions associated with the use of a 3 split fertiliser application suggests that the nitrogen use
399 efficiency was increased. However, the mitigation effect was reasonably small and this might be
400 explained by the fertiliser application relatively early in the growing season. The lower N_2O
401 emissions from the urea 120 application in comparison to the AN 120 application is in agreement
402 with the findings of Dobbie and Smith (2003) and Smith et al. (2012). However, the results of
403 this study must be assessed with caution as ammonia (NH_3) emissions were not measured. Smith
404 et al. (2012) reported that 22 % of urea N applied to arable soil is emitted as NH_3, in comparison
405 to <3 % of ammonium nitrate N. The decrease in N_2O emissions associated with the urea
406 application in this study may therefore be a reflection of greater loss of NH_3 than from the AN
407 treatment resulting in lower soil mineral N concentrations and subsequently decreased potential
408 for N_2O emissions. Evidence for this can be seen in the soil NH_4^+ concentrations where the
409 initially high NH_4^+ concentration in the urea 120 treatment rapidly decreased to lower than the
410 levels seen in the AN 120 treatment, perhaps indicating volatilisation of NH_3. The decreased
411 N_2O emissions associated with the AN 120 (3 splits) and urea treatments were not associated
412 with increased crop yields as may be expected if greater retention of N within the soil was taking
413 place. Again, this supports the suggestion that considerable quantities of N could have been lost
414 in the form of NH_3 from the urea treatment.

415

416 A particularly interesting finding of this research is the significant decrease in crop yield
417 associated with the NI treatments. It was hypothesised that crop yield would be maintained or

418 increased during this experiment due to decreased rates of nitrification and reduced emissions of
419 N_2O and therefore maintenance of higher levels of NH_4^+ in the soil, providing greater N
420 availability for crop growth (Di and Cameron, 2002). However, it has been suggested that plants
421 may preferentially uptake NO_3^- from the soil due to greater ease of transport of NO_3^- through the
422 soil compared with NH_4^+ which is more tightly bound to the soil particles (Hofman and van
423 Cleemput, 2004). If the NI prevented conversion of NH_4^+ to NO_3^- by nitrification, then crop N
424 uptake and growth may suffer. The decrease in crop yield caused by the addition of a NI could
425 have implications for the adoption of NIs as an N_2O mitigation strategy by the farming
426 community, despite the financial benefits for the farmer associated with decreased loss of N
427 through N_2O emissions. The yield results observed in this experiment are in contrast to those
428 demonstrated in previous work in which DCD acted to increase crop or pasture yield (Di and
429 Cameron, 2002; Liu et al., 2013; Pain et al., 1994) or had no effect on crop yield (Weiske et al,
430 2001). The decrease in N_2O emissions combined with the decrease in crop yield observed from
431 the NI treatments resulted in a large (non significant) reduction in yield scaled emissions in
432 comparison to the non NI amended treatments by 31 % for the AN 120 + NI treatment and 40 %
433 for the urea 120 + NI treatment.

434 *4.5 Sampling period effects on N_2O emissions and emission factors*

435 This research demonstrated the considerable contribution of background emissions to emissions
436 recorded from applied treatments. Cumulative emissions from the control treatments represent 43
437 % of annual emissions from the highest N fertiliser treatment and 51 % of emissions from the
438 AN 120 treatment which are within the range of previously reported data. McTaggart et al.
439 (1997) reported background emissions that contributed 75 % of the emissions from spring
440 barley fertilised with 120 kg N ha^{-1}, and Smith et al. (2012) reported 26-67 % contribution of

441 control treatments to emissions from N fertilised treatments. This evidence suggests that
442 background emissions from unfertilised arable crops can be high and represents a considerable
443 proportion of the overall flux from fertilised crops. Smith et al. (2012) suggested that this high
444 background flux from arable sites is due to mineralisation of crop residues which is also likely to
445 have occurred at our experimental site following harvest of the previous oilseed rape crop.

446 Background emissions could also be considered as those occurring after the return of soil mineral
447 N to background levels, which in this experiment occurred during August 2011. Emissions after
448 this time could reflect crop residue inputs, N deep within the soil profile, remineralised fertiliser
449 N or treatment effects from previous fertiliser events, all of which may confound emissions from
450 the treatments of interest. Our work demonstrated the greatest cumulative monthly emissions in
451 August with mean cumulative N_2O-N emissions of 1.35 kg N_2O-N ha^{-1}. Previous research has
452 often not measured N_2O emissions for an entire year. For example, McTaggart et al. (1997)
453 measured emissions from sowing until early June and although Smith et al. (1998a) measured
454 N_2O emissions for a year from fertilisation, measurements were suspended during a period of
455 low fluxes in the summer and resumed again after autumn cultivation. If we had not taken
456 measurements during the summer, this period of high emissions would not have been recorded.
457 The large emissions during the summer months are suggested to be due to underlying natural
458 "background" variation in N_2O fluxes over space and time.

459 Although Bouwman (1996) and the IPCC recommend the use of N_2O emissions data from at
460 least 12 months of measurements in order to calculate EFs to achieve an accurate reflection of
461 management practices, we have calculated EFs over three timescales to analyse the effects of
462 background N_2O emissions on EFs. There were interesting variations between the seasonal and
463 annual EFs with annual EFs (-0.28 – 1.35 %) generally being greater than seasonal EFs (-0.04 –

464 0.86 %) (Table 2) due to the contribution of emissions over the winter period. Calculating EFs
465 over a longer time period did not always result in a greater EF, for example larger EFs were
466 commonly obtained over the 5 week calculation period in comparison to the seasonal period.
467 This is due to control emissions representing a lower proportion of total emissions immediately
468 following fertiliser application, and the subtraction of these from treatment emissions during the
469 EF calculation thereby causes greater calculated EFs. The question of which EF is more
470 appropriate to use depends on the desired outcome. Our findings indicate that, despite most
471 emissions usually occurring during the 5 week period after fertiliser application, the 5 week EF
472 calculation is inappropriate, when environmental conditions (e.g. rainfall and temperature) after
473 this time period are conducive to N_2O production. This work illustrated that there can be further
474 significant N_2O emissions which should be included in EF calculations to accurately reflect N_2O
475 EFs for arable soils. However, the decision to use a seasonal or annual EF is more complex. If it
476 is desirable to calculate an EF which accurately reflects the effects of specific treatments on N_2O
477 fluxes from arable soils then the results of this work suggest that a seasonal EF should be used in
478 order to remove the effects of background N_2O fluxes which are likely to be unrelated to the
479 applied treatments. Seasonal EFs may therefore provide a more accurate indication of the
480 emissions attributable to fertilisation and specific treatments which makes the use of year long
481 EFs for this purpose questionable. However, this would require removal of a large part of the
482 data set, which Smith et al. (2012) suggests would usually decrease the magnitude of calculated
483 EFs by 30 % in comparison to those which include a full year's data.

484 *4.6 Comparison to IPCC "default EF" and previously reported values*

485 The mean EFs calculated in this experiment are considerably lower than the IPCC's standard
486 EF1 value of 1.25 % which is currently applied to much of the UK, and also lower than the new

EF of 1 %. Mean annual and seasonal EFs were calculated for the purpose of comparison to the IPCC standard value and as such only treatments within the normal range of fertilisation were included (AN 80, AN 120, AN 160, Urea 120). In our study the mean annual EF from these treatments was 0.79 % and the mean seasonal EF was 0.56 %. The EFs of the NI amended treatments were lower than the mean annual EF, due to the decreased N_2O emissions associated with these treatments, however the AN (3 splits) treatment EF was higher than the mean annual EF although lower than the EF of the equivalent AN 120 treatment. The AN 120 treatment is representative of the amount of N fertiliser which would be commercially applied in comparable situations in Scotland. The annual EF for this treatment is 1.35 % which is greater than the IPCC Tier 1 EF of 1.25 % or 1 %. Previous research into EFs from spring barley in Eastern Scotland found EFs of 0.6 - 0.7 % (McTaggart et al., 1997; Smith et al., 1998 a,b), demonstrating a much smaller range of EFs than those found in this experiment. It is suggested that the large range of EFs obtained from this experiment are due to the range of fertiliser application rates, intense sampling frequency and unexpectedly large emissions from the control plots. Also, the unusual weather conditions over the study period which involved large amounts of rainfall over the summer months during which time the treatment effects were no longer occurring, resulted in large emissions which were not associated with individual treatments.

Smith et al. (1998a) compared EFs from Scottish arable and grassland sites to the data plotted by Bouwman (1996) and found that N_2O emissions as a proportion of applied N, from the Scottish sites, and in particular from the Scottish arable sites, are generally lower than from the rest of the UK. This difference has been suggested to be due to lower temperatures in Scotland resulting in lower N_2O emissions (Smith et al., 1998a). However, if just the EF calculated for the standard fertiliser application rate (AN 120) is considered, then the EF is higher than the IPCC's 1.25 %

default EF and the new 1 % EF. Again, this is suggested to be due to the unusual weather conditions experienced during the experimental period. Overall, the range of EFs obtained from this experiment appear to support the movement from the IPCC's 1.25 % EF to the 1 % EF when factors such as the climatic conditions are taken into account. It must also be considered that the experiment was only one year in length, and that to obtain a more accurate view of EFs from these treatments, more experiments of this type would be required in order to take into account variables such as soil and climate.

5. Conclusion

This research demonstrated that area based emissions of N_2O are linearly related to N input, supporting the IPCC's approach to calculating EFs. Soil % WFPS was shown to have a significant effect on the magnitude of N_2O emissions and to have greater control over N_2O production than soil mineral N. For this typical Scottish spring barley crop and soil system receiving mineral fertiliser, the optimum fertiliser application rate is 160 kg N ha^{-1}, as indicated by the calculated N_2O emission intensities of all treatments. Emission intensity results also highlight the need to avoid under-fertilisation of crops if crop yields are to be maintained whilst minimising N_2O emissions. The use of a NI, split fertiliser applications and urea instead of AN, showed the potential to reduce N_2O emissions, however, the amendment of treatments with a NI and 3 split treatment also decreased crop yield, raising questions over their suitability as N_2O mitigation options in arable agriculture and prompting the need for further investigation. The importance of the contribution of background emissions to calculated EFs was demonstrated and the need for year long measurements of N_2O emissions is questioned. Calculated annual EFs

were generally lower than the IPCC's default Tier 1 EF of 1.25 % and the new value of 1 %, but largely support movement to, and use of, this new EF value, although further research in other locations is required to assess its suitability for use throughout the UK.

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